Stereospecific Cyclic Ketone Formation with Iron(0): Anatomy of an Interligand Reaction[†]

Edward Weissberger*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

Pierre Laszlo*

Institute de Chimie, Université de Liège, Sart-Tilman par 4000 Liège, Belgium

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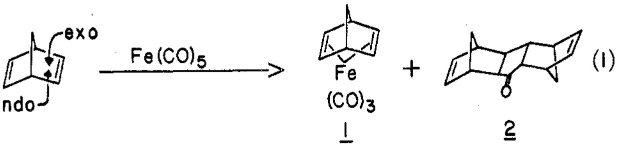
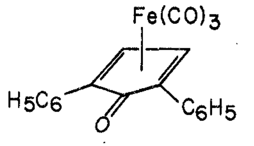
Iron carbonyls play an important role in nature as well as in the laboratory. For example, carbon monoxide poisoning occurs because carboxyhemoglobin is a more stable complex than is oxyhemoglobin. Describing his remarkable discovery of the first metal carbonyl complex, $Ni(CO)_4$, in 1890, Ludwig Mond wrote:[1] "... it is our intention to fully investigate this problem and more particularly to study its action upon organic bodies". This great English chemist and industrialist went on to prepare a variety of metal carbonyls, including $Fe(CO)_5$ in 1891. Thirty-nine years later, Rheilen[2] reported the butadiene complex $C_4H_6Fe(CO)_3$, the first olefin complex of iron in the zero oxidation state.

The role which iron carbonyls play in organic synthesis and in our understanding of metal-induced carbonylation reactions received a major boost in 1958 with the preparation of a stable iron tricarbonyl compound of norbornadiene,[3] **1**, and the nearly simultaneous report[4] in 1959 that a ketone had been isolated from a similar preparation. Indeed, five ketonic and four dimeric products have been isolated from this reaction sequence,[5] although only the ketone illustrated as **2** in reaction 1 has been fully characterized.



The adduct **2** was first assigned as the endo-trans-endo isomer on the basis of an unusual n → π* transition. The depicted exo-trans-exo stereochemistry was correctly assigned to **2** in an early and important application of the Karplus relationship,[6] which relates interproton coupling constants and dihedral angles. This stereochemistry was unequivocally confirmed by a series of elegant alternate syntheses.[7]

Between 1958 and 1971[8] the preparation of cyclopentanones from olefins and iron carbonyls received little attention. However, cyclopentenone synthesis from acetylenes did not languish. Iron complex, **3**, incorrectly formulated as a bis(acetylide)tetracarbonyliron(II) complex in 1955, was correctly described as the cyclopentadienone complex by Schrauzer[9] and by Cotton[10] in 1958. Further, Schrauzer[11] prepared a series of iron complexes containing newly formed carbon–carbon linkages from diphenylacetylene with one, two, and even three iron atoms. Weiss[12] reported that in inert solvents $Fe_3(CO)_{12}$ reacts with acetylene to form a series of iron-containing products, including the iron tricarbonyl derivative of tropolone. This thermal reaction must be contrasted with the thermal reaction of acetylene with $Fe(CO)_5$ in aqueous media which Reppe[13] has reported to form hydroquinone.



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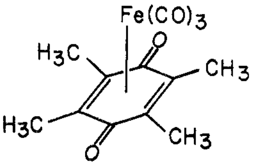

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Historically, the reaction of dimethylacetylene to form duroquinonetricarbonyliron(0), **4**, is particularly interesting as it facilitated a partial test of Longuet-Higgins and Orgel's theoretical prediction[14] that metal complexation could be expected to stabilize cyclobutadiene. Using the Longuet-Higgins–Orgel procedures,

Edward Weissberger was born in 1941 in Rochester, N.Y. He graduated from Brown University and obtained his Ph.D. from Stanford University, studying the chemistry of excited atomic oxygen with Professor H. Taube. After postdoctoral study with Professor J. P. Collman and a term at the University of California at Santa Cruz, he returned east in 1969 as Assistant Professor of Chemistry at Wesleyan University. His research interests include metal-induced organic skeletal transformations and atomic chemistry. In addition to chemistry, he enjoys history, mountains, and marine life, using his skills as a pilot to visit out-of-the-way places.

Pierre Laszlo, born in Algiers in 1938, attended the Sorbonne where he obtained his D.Sc. with Professor E. Lederer. He then went to Princeton University to do postdoctoral work with Professor Paul von R. Schleyer. After being an instructor in Orsay, he was an Assistant Professor at Princeton and now holds the chair of physical organic chemistry at the University of Liège. Besides the topic of this article, his current research interests include molecular dynamics of globular systems, sodium-23 NMR, and new modes of addition of cyano olefins. He is strongly attracted by epistemology and philosophy.

[†] To the memory of a great scientist, Ernst A. Koerner von Gustorf.

(1) L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, 749 (1890).

(2) H. Rheilen, A. Gruhl, G. V. Hessling, and P. Pfrengle, *Justus Liebigs Ann. Chem.*, **482**, 161 (1930).

(3) R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *Chem. Ind. (London)*, 1592 (1958).

(4) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

(5) (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960); (b) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 368 (1961); (c) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *ibid.*, 372 (1961).

(6) M. Green and E. A. C. Lucken, *Helv. Chim. Acta*, **45**, 1870 (1962).

(7) R. C. Cookson, J. Henstock, and J. Hudec, *J. Am. Chem. Soc.*, **88**, 1059 (1966).

(8) Y. Menachem and A. Eisenstadt, *J. Organometal. Chem.*, **33**, C29 (1971).

(9) G. M. Schrauzer, *Chem. Ind. (London)*, 1404 (1958).

(10) (a) F. A. Cotton and J. R. Leto, *Chem. Ind. (London)*, 1592 (1958); (b) J. R. Leto and F. A. Cotton, *J. Am. Chem. Soc.*, **81**, 2970 (1959).

(11) (a) G. N. Schrauzer, *Chem. Ind. (London)*, 1403 (1958); (b) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959).

(12) W. Hübel and E. Weiss, *Chem. Ind. (London)*, 703 (1959).

(13) W. Reppe and H. Vetter, *Justus Liebigs Ann. Chem.*, **582**, 133 (1953).

(14) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

Sternberg, Markby, and Wender[15] predicted the stability of quinone–metal complexes and experimentally confirmed their prediction. Later, iron tricarbonyl derivatives of tetraphenylcyclobutadiene[16a] and of cyclobutadiene[16b] itself were prepared. The dimer of dichloro(tetramethylcyclobutadiene)nickel(II)[16c] served as the first direct confirmation of the prediction.

It rapidly became apparent that the three common iron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, induce similar although not always identical chemistry; yet their reactivities differ greatly. Often $Fe(CO)_5$ is found to be less reactive than $Fe_2(CO)_9$ under thermal conditions, while, unlike reactions with $Fe_2(CO)_9$, those of $Fe(CO)_5$ are subject to photochemical initiation.

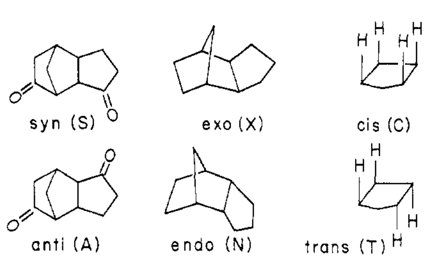
Thoughtful, comprehensive reviews of metal carbonyl chemistry[17,18] adequately describe salient features as they had been registered by the early 1970's. In this Account we shall discuss results which have been obtained in our laboratories and those of other investigators during the past 5 years, emphasizing the use of iron carbonyls and the understanding of their reactions with strained unsaturated rings. Two processes leading to cyclic ketones are presented. The first and more extensively studied process is a coupling reaction in which *olefin cycloaddition takes place with carbonyl insertion* so as to stereospecifically generate cyclopentanones related to ketone **2**.[19-22] Not only is the overall pathway[21] of this process understood, but also the reaction illustrates unusual features such as efficient enantiomeric recognition.[22] The second process considered is the newly demonstrated stereospecific ring expansion[23] of α-pinene and β-pinene, a process giving rise to isomeric but skeletally enantiomeric ketones.

The power of stereochemical arguments in unraveling the mechanism of complex organometallic reactions has been expressed cogently in pioneering studies such as those of Whitesides.[24]

As we shall see, one great advantage of employing stereochemically rigid reagents is that product stereochemistry may be used to elucidate details of reaction pathways. This article will also illustrate the power of modern spectroscopic tools[25] to pick the correct stereoisomer out of a large number of related structures.

Possible Cyclic Products

Inspection of reaction 1 shows that there are in fact six isomers possible for the cyclopentanone product. When the degree of symmetry within and between the reagents is reduced, the number of possible structures increases. Formation of a substituted cyclopentanone through coupling of two different olefins to one another and to a carbon monoxide unit may lead to a large number of structures. In the absence of symmetry restrictions there are $2^6 = 64$ structures, some of which will contain planes of symmetry and others of which will be enantiomeric. If the olefins each contain a symmetry plane bisecting the double bond undergoing coupling, thus removing "front–rear" differentiation, the structure count reduces to $2^4 = 16$. Equivalently, there are 2^4 structures possible when the two bonds formed on each olefin must be from the same face, as in norbornyl couplings. When both these restrictions obtain, the structure count is further reduced to $2^3 = 8$. Finally, if in addition to these restrictions the coupling olefins are identical, there are $2^3 - 2 = 6$ possible isomers. This is the case in cyclopentanone formation from norbornene.

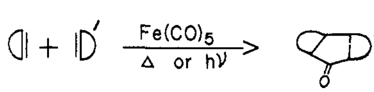


Incorporation of carbon monoxide into a single generalized olefin leads to a far simpler situation. The two newly formed bonds which connect the added CO to any two specific centers of the olefinic molecule lead to a total of $2^4 = 16$ stereoisomers. The number of structures is reduced to $2^3 = 8$ if *both* of the coupling centers are the olefinic carbons themselves.

Specific cases of external and internal cyclization will now be discussed with knowledge that a variety of isomeric products are possible. As a consequence of the remarkable stereospecificity of iron(0) we generally obtain only one product, making both cyclopentanone formation and ring expansion using iron(0) as the carbonylating agent a synthetically useful process. Further, the use of stereorigid reagents has allowed us to draw mechanistic conclusions not otherwise available.

Cyclopentanone Formation

The generic reaction illustrated as reaction 2 leads to synthetically useful yields of cyclopentanone derivatives from strained olefins.[19-22] The presence of electron-withdrawing groups as in methyl acrylate[26] (**16**) improves reactivity. A number of examples are illustrated in Figure 1.



(2)

Although $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ may be used as coupling reagents, our desire to use the simplest and least expensive possible reagent in order to keep the cost of a potentially useful synthetic procedure at a minimum led to $Fe(CO)_5$ as the principal reagent. The simplicity inherent in the geometry of $Fe(CO)_5$, a trigonal bipyramid, facilitates analysis of the stereochemical outcome. When two carbon monoxide units are replaced by two ligands L and L′, for instance, an olefin or a π-allyl group, three isomeric structures may

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(15) H. W. Sternberg, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **80**, 1009 (1958).

(16) (a) W. Hübel and E. A. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); (b) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965); (c) R. Criegee and G. Schröder, *Justus Liebigs Ann. Chem.*, **623**, 1 (1959).

(17) (a) G. N. Schrauzer, *Adv. Catal.*, **18**, 373 (1968); (b) P. Heimbach, *Angew. Chem., Int. Ed., Engl.*, **12**, 975 (1972); (c) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

(18) E. Koerner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1970).

(19) (a) J. Mantzaris and E. Weissberger, *Tetrahedron Lett.*, 2815 (1972); (b) A. Speert, J. Gelan, M. Anteunis, A. P., Marchand, and P. Laszlo, *ibid.*, 2271 (1973); (c) L. Lombardo, D. Wege, and S. P. Wilkinson, *Aust. J. Chem.*, **27**, 143 (1974).

(20) J. Mantzaris and E. Weissberger, *J. Am. Chem. Soc.*, **96**, 1873 (1974).

(21) J. Mantzaris and E. Weissberger, *J. Am. Chem. Soc.*, **96**, 1880 (1974).

(22) (a) J. Grandjean, P. Laszlo, and A. Stockis, *J. Am. Chem. Soc.*, **96**, 1622 (1974); (b) E. Weissberger and G. Page, to be published.

(23) A. Stockis and E. Weissberger, *J. Am. Chem. Soc.*, **97**, 4288 (1975).

(24) G. M. Whitesides and P. E. Kendall, *J. Org. Chem.*, **37**, 3718 (1972).

(25) P. Laszlo and P. J. Stang, "Organic Spectroscopy. Principles and Applications", Harper and Row, New York, N.Y., 1971.

(26) F.-W. Grevels, D. Schulz, and E. Koerner von Gustorf, *Angew. Chem., Int., Ed. Engl.*, **13**, 534 (1974).

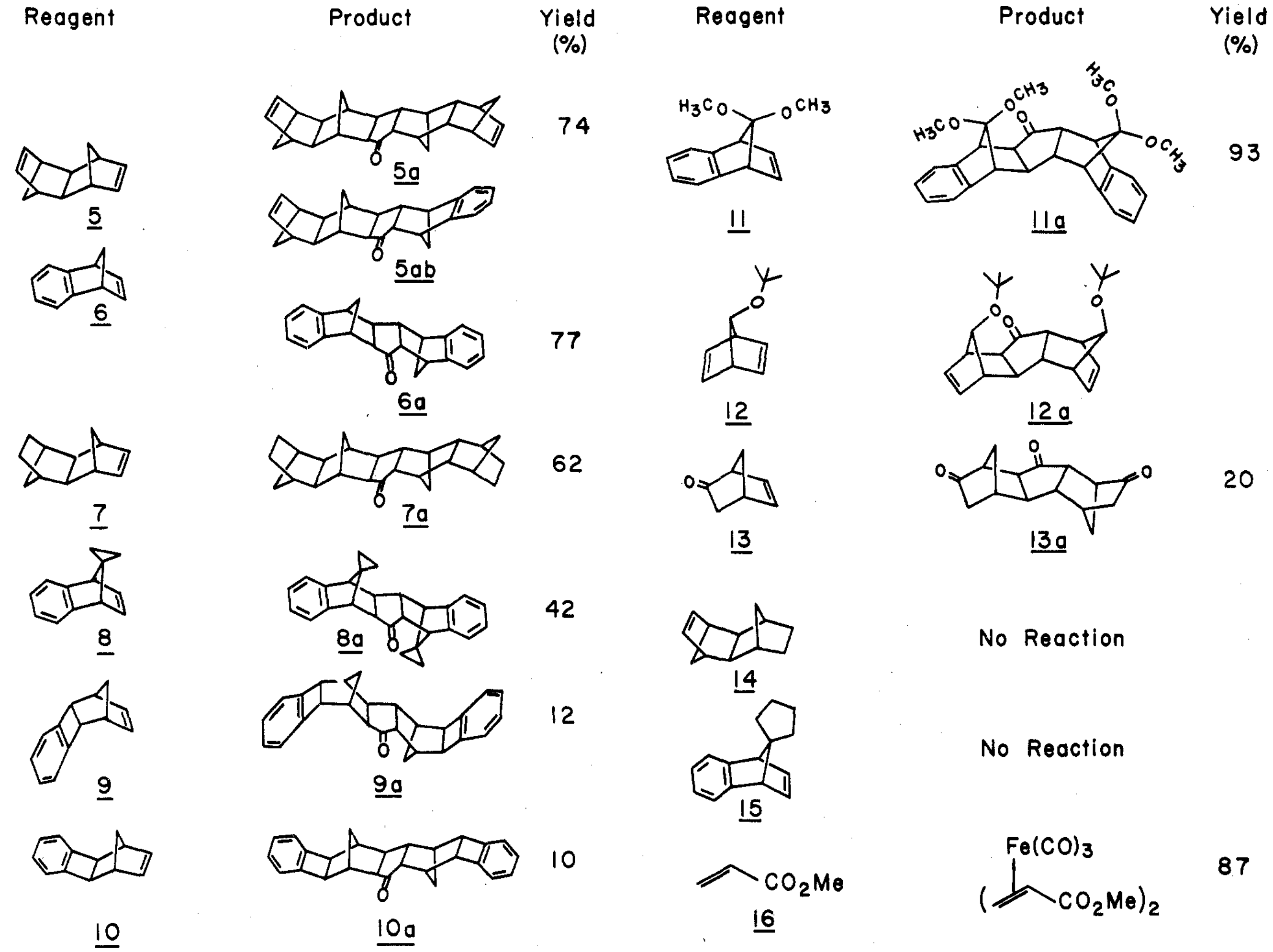

Figure 1. Coupling reactions. Reported yields are not maximized nor do they refer to standard conditions.

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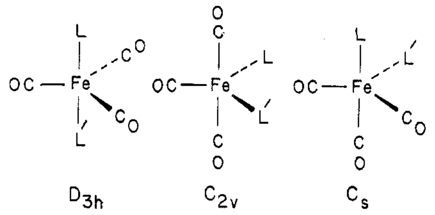
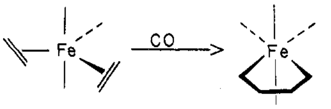


The coupling L + L′ + CO is best achieved when L and L′ are both in the basal plane with the olefin π^* orbitals also in this plane and local C_{2v} symmetry about the iron center. In the D_{3h} conformation, there can be no bonding interaction between olefinic ligands L and L′ as they are too distant from one another, while L–L′ overlap is greater in the C_{2v} conformation than in the C_s conformation. In the C_{2v} conformer the proximal ends of each olefinic ligand are pointed toward one another so as to bring about ring closure to a five-membered metallocycle centered on iron, while in the C_s conformer the ligand orbitals are perpendicular to one another.



Osborn[27a] and Hoffmann[27b] have discussed the geometries and intramolecular rearrangements in pentacoordinate d^8 transition-metal compounds concluding that strong π acceptors such as CO and monoolefins prefer basal coordination while strong σ donors prefer axial coordination. In the case of tricarbonylbis(olefin)iron(0) intermediates both ligand types are strong π acceptors, making differentiation between coordination sites on this basis inconclusive. However, as Osborn points out, steric interactions between ligands decrease as bulky ligand coordination goes from basal–axial to basal–basal. The olefin ligands with which we are dealing are sterically bulky, leading to preferential formation of the C_{2v} structure. Furthermore, maximum bonding between the metal donor orbitals and the olefin acceptor π^* orbitals is achieved when the olefins themselves are in the basal plane. While arguments similar to these may be advanced for square-pyramidal geometries, no such deviation from the trigonal-bipyramidal geometry has been reported for Fe(0) complexes having only unidentate ligands. Confirmation of the preferred C_{2v} structure has been obtained by Koerner von Gustorf[26] who reported that the infrared spectrum of tricarbonylbis(methyl acrylate)iron(0) indicates C_{2v} symmetry.

Unlike simple olefin cycloadditions, reactivity and product stereochemistry are invariant upon changing from thermal to photochemical initiation when $Fe(CO)_5$ is the coupling agent. Inert solvents such as n-hexane, n-heptane, or n-octane may be used for the photolytic[21] or the thermal[22] experiments under an inert atmo-

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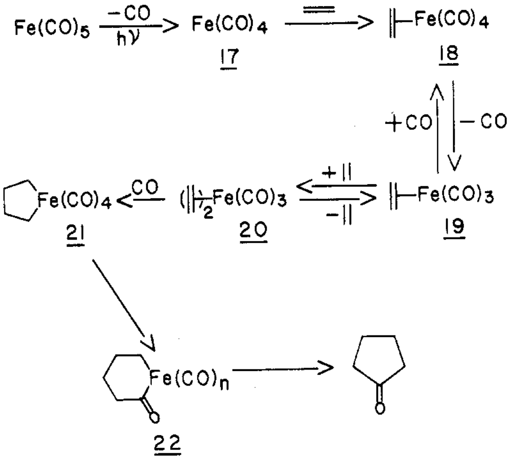
(27) (a) J. R. Shapley and J. A. Osborn, *Acc. Chem. Res.*, **6**, 305 (1973); (b) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975); (c) R. Hoffmann and M. Elian, *ibid.*, **14**, 1073 (1975).

Scheme I
Olefin Coupling



sphere; thermal experiments may also be carried out neat. The iron-rich deposit which forms during both thermal and photochemical reactions should be treated with respect as it is mildly pyrophoric. Normal filtration and chromatographic procedures are applicable in all cases.

Olefin Coordination

The initiating step must necessarily involve occupancy by an olefin of a vacant coordination site on the metal made available by prior loss of CO, as in Scheme I. Considerable data now exist indicating that the formation constants of olefin–metal linkages increase dramatically with decreasing olefin stability. This is reflected in the improved binding of olefins to metals as olefin ring strain increases. Noting the relative binding of olefins to group 1B metals, one would predict a similar sequence for the coordination of cyclic olefins to iron carbonyls, viz., cyclohexene < cyclopentene < cycloheptene < norbornadiene, norbornene[28,29] despite bonding differences between group 1B olefin–metal complexes and group 8 olefin–metal complexes. Olefin reactivity toward $Fe(CO)_5$ appears to follow the same order.[19a,20,21]

π complexes are formed between bicyclic olefins and metal centers from the endo or the exo side. In general, the latter prevails. For instance, norbornadiene suffers exo complexation by Cu(I),[30,31] Cu(II),[32] Ag(I),[33] and Au(I).[34] Usually norbornene displays exo coordination, although the presence on the bridge carbon of geminal methyl groups drives complexation to the endo side.[28,29,35,36] Likewise, α- and β-pinene are coordinated on the endo side due to steric hindrance on the exo side. Thus, group 1B and other transition metals complex monoolefins primarily from the less hindered side. One cannot but notice the strong similarity between the iron carbonyl induced coupling of olefins and the Cu(I)-catalyzed olefin photodimerization discovered by Salomon and Kochi[37] who report obtaining exo-trans-exo norbornene photodimers in 79% yield with formation of only minor amounts of the exo-trans-endo stereoisomer. Further evidence for exo-iron binding in these reactions is gained from lack of reactivity of **15**, in spite of smooth couplings of **6** and **8**.

A special case arises when another potential ligand such as an atom having a lone pair of electrons is accessible to the metal center. Exo coordination will be reinforced if the Lewis base is on the exo side, while the delicate exo–endo balance may be shifted to the endo side if the Lewis base occupies a suitable endo position. This influence of a Lewis base substituent at the bridge position is striking. Even though a total of six diastereomeric structures could conceivably be generated, a single product with the syn-exo-trans-endo-syn stereochemistry is obtained in better than 90% yield[19b] when 7,7-dimethoxybenzonorbornadiene (**11**) dimerically couples to cyclopentanone **11a**.

Olefin coordination assumes the transient presence of $Fe(CO)_4$. Tetracarbonyliron(0), which once evoked great controversy, has now been firmly characterized,[18,38] there being no doubt that it is the reactive species photolytically generated from $Fe(CO)_5$. While details of the thermal reaction may differ from those of the photolytically initiated reaction, the two processes are thought to be essentially the same. In the absence of a trapping olefin, $Fe(CO)_4$ leads efficiently to $Fe_2(CO)_9$. In octane solution this process occurs even under an atmosphere of CO, as reversal to $Fe(CO)_5$ is relatively inefficient. Reactive olefins block formation of highly insoluble $Fe_2(CO)_9$ through the formation of monoolefin complex **18** (Scheme I). Even relatively unreactive olefins such as cyclohexene, cyclopentene, and **14**, which *do not form* appreciable amounts of ketonic products, are quite effective in retarding $Fe_2(CO)_9$ formation.[20,21] Complexation of poorly coupling olefins is an important observation, as it allows the demonstration of ligand exchange (vide infra). The reaction continues to proceed via a series of coordinatively saturated and unsaturated iron complexes. Reaction inhibition by external CO is accounted for by the reversible loss of CO from monoolefintetracarbonyliron(0) complex **18**[21] which makes available a vacant coordination site on the metal. Working with methyl acrylate (**16**) as the reactive olefin, Koerner von Gustorf and his collaborators demonstrated the photochemical loss of CO at this stage.[26] They were able to isolate and characterize intermediates corresponding to monoolefin **18**, bisolefin **20**, and metallocycle **21**. Infrared data consistent with coordinatively unsaturated complex **19** suggest an appreciable concentration of this species.

Even with a poorly complexing olefin such as cyclohexene, intermediate **18** is formed and serves to store the reactive iron species. When photolysis is carried out with excess cyclohexene as the only olefin present, neither ketonic product nor $Fe_2(CO)_9$ is formed. If the lamp is extinguished and a reactive olefin such as benzonorbornadiene (**6**) is added, cyclopentanone (**6a**) rapidly appears. *The reactive olefin has replaced the unreactive olefin in the metal coordination sphere.*

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(28) J. M. Harvilchuck, D. A. Aikens, and R. C. Murray, *Inorg. Chem.*, **8**, 539 (1969).

(29) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev. Chem. Soc.*, **12**, 265 (1968).

(30) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).

(31) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1889 (1973).

(32) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *Inorg. Chem.*, **5**, 1399 (1966).

(33) R. A. Zelonka and M. C. Baird, *J. Organometal. Chem.*, **33**, 267 (1971).

(34) R. Hüttel, H. Reinheimer, and H. Dietl, *Chem. Ber.*, **99**, 462 (1966).

(35) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **92**, 201 (1970); H. C. Brown and K. T. Liu, *ibid.*, **93**, 7335 (1971).

(36) W. C. Baird and J. H. Surridge, *J. Org. Chem.*, **37**, 304 (1972).

(37) R. G. Salomon and J. K. Kochi, *Tetrahedron Lett.*, 2529 (1973); *J. Am. Chem. Soc.*, **96**, 1137 (1974).

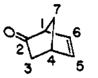
(38) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Am. Chem. Soc.*, **85**, 1013 (1963).

When $Fe(CO)_5$ photolysis is carried out under an atmosphere of carbon monoxide in the presence of a reactive olefin, product formation is strongly retarded. If after a standard time period the lamp is extinguished and CO is purged from the reaction vessel with N_2, product rapidly appears. Oxidative coupling and migratory insertion steps are generally thought to occur with kinetic or at least thermodynamic ligand assistance. Nevertheless, due to the necessity of vacating a coordination site in order to accommodate a second molecule of olefin, carbon monoxide has an overall inhibitory effect on the reaction. This observation permitted us to demonstrate that formation of bisolefintricarbonyliron(0) intermediate **20** is a thermodynamically controlled equilibrium process.[21]

Crossing experiments were used to demonstrate the equilibrium formation of **20.** Olefin **6** was added to $Fe(CO)_5$ in *n*-octane under an atmosphere of CO, and the solution was photolyzed for the standard 0.5 h. Upon cessation of photolysis, an equimolar amount of **5** was added, CO purged from the system, and a product analysis carried out. Ketones **6a** and **5ab** were observed in the ratio 2:1, with a relative yield of less than 1% for ketone **5a.** When the inverse experiment was performed, with addition of **5** *followed* by addition of **6** after photolysis, the same product ratios were observed. Hence, bisolefin intermediate **20** defines a mixture of species whose relative proportions are determined by the olefin–metal binding constants.

Substituent Effects

Having analyzed the reaction steps leading to the bisolefin intermediate **20,** we may now turn our attention to its transformation into the final products. Details of the carbon–carbon bond forming steps were probed by comparing possible and observed products as functions of structural variation in the reactant. In order to complement the stereochemical data obtained with norbornene itself, we studied cyclopentanone formation from 2-norbornenone (**13**), where the presence of the distant carbonyl substituent polarizes the carbon–carbon double bond through homoconjugation.[41]



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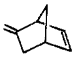
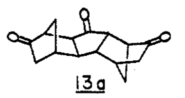


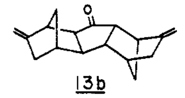
13′

The carbonyl group of norbornenone distinguishes the front from the rear of the molecule and induces a difference in the electron densities at C-5 and C-6 as measured by the 12.2-ppm chemical shift difference between these two carbons observed in the ^{13}C NMR spectrum. This difference allows the metal to discriminate between C-5 and C-6 (vide infra). A *single* racemic product is obtained from reaction of 2-norbornenone (*R,S*) with $Fe(CO)_5$ in refluxing *n*-heptane, a reaction which could conceivably lead to 20 isomers, 4 of which are meso and 16 of which represent enantiomeric pairs, as has been previously discussed.[22a]

Extrication from this stereochemical maze was greatly facilitated by the inherent high resolution of carbon magnetic resonance spectroscopy. Observation of only eight carbon resonances for the observed $C_{15}H_{16}O_3$ adduct implied the presence in the molecule of seven pairs of carbon atoms related by either a twofold rotation axis or a mirror plane in addition to the lone carbonyl carbon on that symmetry element.[22a,39] On this basis, only 8 of the 20 structures need be considered further. The magnitude of the interproton coupling constants[22a] derived from the 300-MHz ^{1}H NMR spectrum restricted consideration to the two exo-trans-exo enantiomeric pairs: that with both norbornyl carbonyls syn to the cyclopentanone carbonyl and that with both anti. Final adduct differentiation was made by measuring the dipole moment. The calculated values are 4.5 ± 0.7 D for the fully syn adduct and 1.5 ± 0.5 D for the fully anti adduct, with 4.6 ± 0.3 D being observed. The adduct formed is thus the syn-exo-trans-exo-syn stereoisomer **13a** and its enantiomer, in which C-5 has coupled to C-5′ while C-6 and C-6′ have coupled to CO. Formation of the C_2 symmetric product implies enantiomeric recognition during the reaction such that only norbornenone enantiomers of like absolute configuration couple to one another. Beyond starting material and polymers, this was the only organic material isolated by column chromatography from the reaction mixture. Polarization of the C═C bond by the norbornenone C═O directs the metal–carbon bond formation exclusively to C-6 rather than to C-5.



13a



13b

Although early use of molecular orbital arguments in explaining observed organometallic reactions suffered from overly simplifying arguments, such as the assumptions of concerted reactions and the absence of metallocyclic intermediates, Hoffmann[27b,c] and others have shown the power of such considerations when properly applied. Without implying quantitative relations, we are able to understand the coupling of 2-norbornenone in terms of a relatively simple description. This description is based on relative thermodynamic energies of possible bisolefin intermediates. The importance of a bisolefintricarbonyliron(0) intermediate has already been demonstrated. In this discussion, we must account for two experimental facts. First, the cyclopentanone forming reaction is enantiospecific; second, the fully syn product is observed while the fully anti product is not.

Consideration of bonding between olefin C═C orbitals and appropriate metal d orbitals allows one to understand the exclusive generation of a syn-syn product. As expected, INDO calculations performed on 2-norbornenone show that the wave function coefficient of the olefin π^* orbital is far greater at C-5 than at C-6. Consequently, as illustrated, strong C–C interaction develops when the C-5 carbon atoms are adjacent to one another in the bis-olefin intermediate. While to a first approximation the isolated olefin–metal interactions remain constant when this situation is reversed, interligand bonding is drastically reduced lowering overall complex stability. Thus, the intermediate which leads directly to the fully syn product is that of maximum stability. Furthermore, as this intermediate shows

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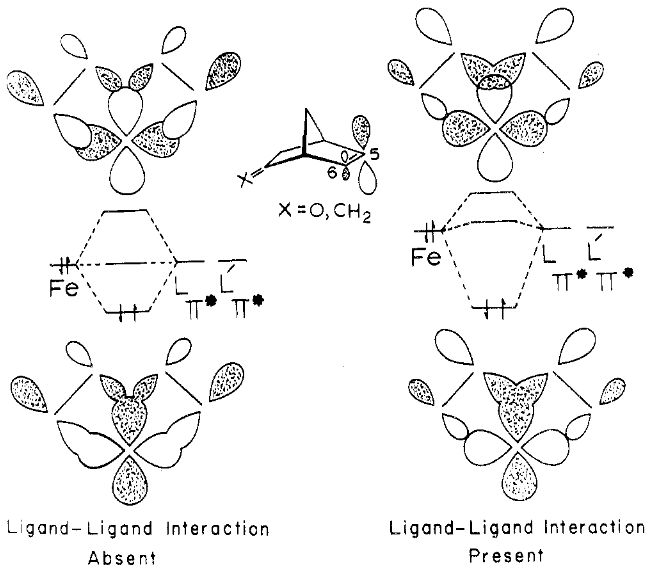
(39) M. Farina and G. Di Silvestro, *Tetrahedron Lett.,* 183 (1975).

(40) (a) A. P. Marchand, B. R. Hayes, D. van der Helm, and S. C. Neely, Abstracts of Papers, 1st North American Chemical Congress, Mexico City, Mexico, 1975; (b) S. E. Ealick and D. van der Helm, *Cryst. Struct. Commun.,* 4, 369 (1975).

(41) This feature was already known for bicycloocten-2-one, a very similar compound: H. Labhart and G. Wagniere, *Helv. Chim. Acta,* 42, 2219 (1959).

maximum C–C overlap, the least activation barrier must be overcome in metallocycle formation from this same intermediate.



Ligand–Ligand Interaction Absent

Ligand–Ligand Interaction Present

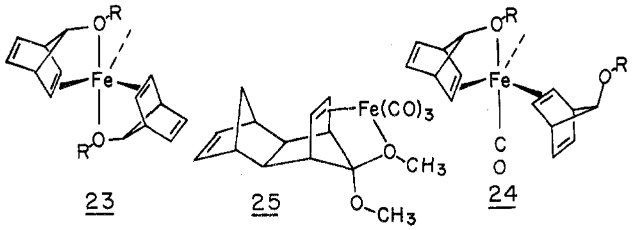
A second case of enantiomeric recognition was recently observed[22b] when racemic 2-methylenenorbornene (**13′**) was treated with $Fe(CO)_5$. Only one racemic product, **13b**, was obtained, this having the illustrated syn-exo-trans-exo-syn stereochemistry. While 2-norbornenone and 2-methylenenorbornene are isoelectronic, they differ in that the hydrocarbon does not contain the highly electronegative oxygen atom. The resulting minimal polarization of the reactive double bond is shown by the small, 2.1 ppm, chemical shift difference between C-5 and C-6. Nevertheless, the reaction is once again enantiospecific and the stereochemistry of the cyclopentanones derived from these two systems is the same. As anticipated by this experimental result, an INDO calculation on 2-methylenenorbornene showed the coefficient of the acceptor π^* orbital to be larger at C-5 than at C-6 just as was found for 2-norbornenone. Thus, we must conclude that enantiospecificity is primarily a consequence of properties of the unoccupied π^* orbital and not the occupied π orbital.

Koerner von Gustorf has shown that bisolefin complex **20** derived from methyl acrylate contains both olefinic ligands in the basal plane of the local C_{2v} structure,[26] as had been postulated on the basis of the above-mentioned stereochemical results. The exclusive observation of trans products from cyclopentanone formation where metal chelation is not possible, along with the lack of reactivity of **15**, indicates iron bonding from the exo side. Based upon the observation of trans products, the two strained-ring olefins must be antiparallel to one another prior to oxidative coupling. Such a configuration minimizes steric interaction with the axial CO ligands.[21] Formation of metallocycle **21** from such an exo-antiparallel-exo structure locks the system in the exo-trans-exo isomeric form. We have thus ascertained that the experimental results are consistent with the idea that bisolefin complex **20** has indeed the C_{2v} geometry postulated above as being conducive to the appearance of the five-membered metallocycle **21**.

The final transformation (Scheme I) of **20** into the cyclopentanone product, via species **21** and **22**, has a counterpart in the iridium-induced coupling of norbornadiene reported by Osborn.[42]

Another important clue to the mechanism came from the shift in the stereochemistry of the cyclopentanones with introduction at the norbornyl bridge position of groups capable of competing with the double bond as ligands for the metal center. Presence of a syn alkoxy group on the 7-bridge position in **11** and **12** leads to exclusive formation of exo-trans-endo adducts.[19b,40] The stereochemistry of adduct **12a** has been confirmed by an x-ray structure determination.[40b]

Insertion of carbon monoxide would seem to involve a CO ligand originally in the apical position.[22] When both apical positions can be occupied by other ligands, as in **23**, the bisolefin complex related to **20** is unable to proceed to product. When a syn alkoxy group is present at the norbornyl bridge position, endo complexation of one of the olefinic moieties is required to maintain an apical CO and permit insertion, thus leading to the observed exo-trans-endo adducts[19b,40] through **24**. Alternatively, a species such as **23** might be prevented by its rigidity from undergoing oxidative coupling. A monoolefin–chromium complex corresponding to **23** has been isolated and characterized by Australian workers,[43] while the notion that an appropriately disposed methoxy substituent may displace a carbonyl ligand from iron is substantiated by the isolation[44] of iron tricarbonyl adduct **25**.



23 25 24

Chiroptic Properties of Ketone 5a

The resolution of **5a** further confirms the trans stereochemistry of this molecule whose high rotatory power[45] is noteworthy. Physically isolated from other π systems, the carbonyl chromophore must be described as inherently achiral, implying that the molar absorptivity and the rotatory power of the $n \rightarrow \pi^*$ transition will be similar to other isolated ketone transitions. The inherent achirality of this chromophore is experimentally indicated by an observed molar absorptivity of 43 at 311 nm. Nevertheless, a molecular rotation of $[\phi]_D$ 899° and a molecular ellipticity of $\theta_{max} = 1.0 \times 10^5$ are more typical of inherently chiral systems such as hexahelicene.

A full explanation of the high rotatory power of **5a** is not yet available, although two reasonable explanations have been offered.[45] A back octant projection made with the assumption of cyclopentanone ring planarity shows all of the perturbing atoms to lie in octants of the same sign. Analogous systems with so many rigidly disposed perturbing atoms have not been reported, making it difficult to predict the rotatory power which this should impose other than to say that it should be high. An al-

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(42) A. R. Fraser, P. H. Bird, S. A. Gegman, J. R. Shapley, R. White, and J. A. Osborn, *J. Am. Chem. Soc.*, **95**, 579 (1973).

(43) D. Wege and S. P. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1335 (1972).

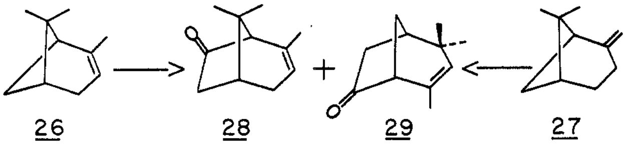
(44) P. Laszlo and A. Stockis, unpublished results.

(45) E. Weissberger, *J. Am. Chem. Soc.*, **96**, 7219 (1974).

ternate potential influence may be nonplanarity of the cyclopentanone ring. Numerous studies have shown that cyclopentanones are generally not planar,[46] although in the case of **5a** nonplanarity would be opposed by the resultant distortion of the norbornyl rings. The unexpectedly high rotatory power of a series of hexahydroindanones has been interpreted[47] as arising from ring nonplanarity, although the quantitative relationship between rotatory power and nonplanarity is uncertain. Nevertheless, the importance of ring nonplanarity is made less likely by a recent x-ray crystal structure determination made on ketone **12a**[40b] whose cyclopentanone ring was found to be nearly planar. The physical properties of this highly strained system whose n → π* uv spectrum is resolved into five components in cyclohexane[45] even at room temperature remain poorly understood and subject to further investigation.

Ring Expansion

Intramolecular analogs to the cyclopentanone-forming reaction also show promise of synthetic utility. Once again the use of sterically rigid reagents has led to mechanistic information. With conjugated dienes as substrates, stable diene–$Fe(CO)_3$ complexes are formed.[17,18] Nonconjugated dienes usually isomerize to the conjugated isomers, forming similar complexes. When such isomerization is blocked, complexation and cyclopentanone formation may be competitive reactions, as is observed with norbornadiene. By studying olefins in which a cyclobutane ring is present, we found another highly stereospecific carbonylation process. As described in the introduction, internal CO insertion may lead to a maximum of 16 stereoisomers. The ring expansion of α- and β-pinene, **26** and **27** respectively, illustrated in reaction 3, is such a case. Prior to our consideration of these vinylcyclobutane derivatives, an interesting series of vinylcyclopropanes[48] and a divinylcyclobutane[49] had been ring opened with $Fe(CO)_5$ and $Fe_2(CO)_9$ forming metal complexes. Illustrated in Figure 2, unusual iron tricarbonyl derivatives had been prepared[50–52] in addition to the formation of cyclohexenone.[52]



(3)

Again, the use of rigid bicyclic reagents leads to products whose stereochemistry is indicative of the reaction pathway. Further, the pinenes have the important added feature that they are chiral and readily available with high enantiomeric purity. Thus chiroptic properties of ketonic products may be used to investigate details of reaction pathways.

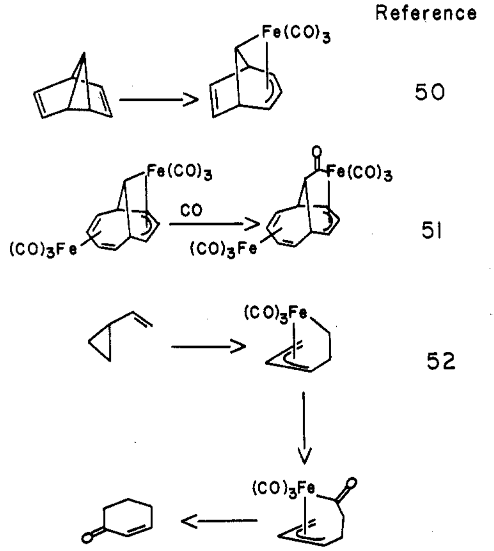


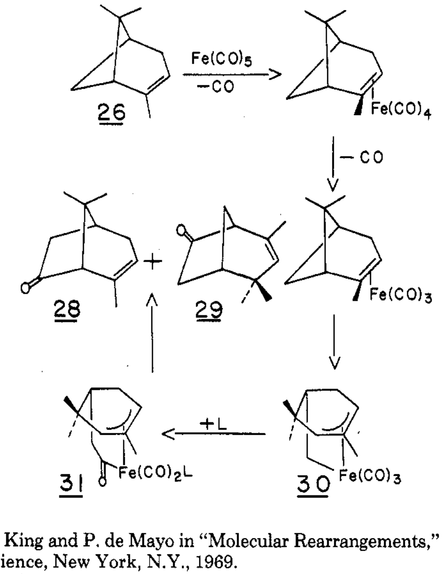
Figure 2. Vinylcyclopropane ring opening and expansion.

Pinene chemistry generally involves cleavage of the linkage bearing the geminal methyl groups[53] so as to form a π-allyl system having C_s symmetry with resultant racemization. This is in contrast to the $Fe(CO)_5$-catalyzed isomerication of β-pinene to α-pinene which was shown by Spanninger and von Rosenberg[54] to occur with 97% enantiomeric retention, although the isomerization yield was only moderate.

Treatment of either pinene with $Fe(CO)_5$ at 160° for 68 h followed by vacuum distillation gave α-pinene and a mixture of two isomeric, skeletally enantiomeric ketones[23] which are formed with maintenance of configurational integrity and may be separated by gas chromatography and by preparative high-pressure liquid chromatography. Structural conclusions illustrated in reaction 3 are based upon ^{1}H NMR, mass, ultraviolet, and circular dichroic spectroscopy.

Ring expansion is controlled by the active iron moiety, as illustrated in Scheme II. If either thermal or

Scheme II
Expansion of (−)-α-Pinene



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(46) (a) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959); (b) H. Kimal and W. D. Gwinn, *J. Chem. Phys.*, **51**, 1815 (1969); (c) H. Howard-Lock and G. W. King, *J. Mol. Spectrosc.*, **36**, 53 (1970).

(47) M. J. Brienne, A. Heymers, J. Jacques, G. Snatzke, W. Klyne, and S. R. Wallis, *J. Chem. Soc. C.*, 423 (1970).

(48) For a review of this literature see ref 23 and references cited herein; see also C. V. Smith and W. E. Billups, *J. Am. Chem. Soc.*, **96**, 4307 (1974).

(49) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **95**, 3798 (1973), and references cited therein.

(50) R. M. Moriarty, Y. C. Ling and K. C. Ramey, *J. Am. Chem. Soc.*, **93**, 6709 (1971).

(51) R. Aumann, A. H. J. Wang, and I. C. Paul, *J. Organometal. Chem.*, **69**, 301 (1974).

(52) (a) R. R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4253 (1970); (b) R. Aumann, *J. Am. Chem. Soc.*, **96**, 2631 (1974).

(53) J. F. King and P. de Mayo in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N.Y., 1969.

(54) P. A. Spanninger and J. L. von Rosenberg, *J. Org. Chem.*, **34**, 3658 (1969).

(55) L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York, N.Y., 1973.

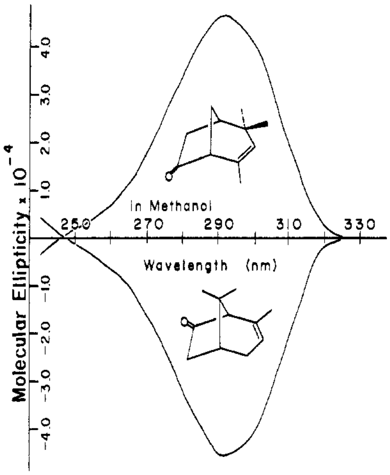

Figure 3. Circular dichroic spectra; ketones from (+)-α-pinene.

metal-induced butane ring opening were occurring with rupture of the bond bearing the geminal methyl groups, as in the general case, incorporation of CO would generate enantiomeric ketones having the geminal methyls adjacent to the carbonyl group rather than generating the isomeric ketones observed. Just as the spiropentyl function of **15** prevents exo iron attack on the norbornyl ring system, so does the syn-geminal methyl group located over the six-membered ring prevent iron attack on the olefinic linkage from the side bearing the geminal methyl groups. Initial complexation of the highly reactive iron carbonyl intermediate is forced to take place from the endo side. As indicated in Scheme II, formation of a vacant coordination site on the iron leads to ring opening and formation of a chiral σ, π-allyl intermediate, **30.**

Following migratory insertion of the nascent carbonyl function, to form intermediate **31**, a process similar to the formation of acyl metallocycles derived from vinylcyclopropanes,[56,57] ring closure may take place to either side of the plane bisecting the π-allyl system. This leads to the formation of two isomeric ketones, each generated with maintenance of configurational integrity. The proposed pathway carries with it a set of predictions which may be experimentally considered as tests of its validity. First, as the two ketones, **28** and **29**, are proposed to be β,γ unsaturated and formed with maintenance of configurational integrity, they will be inherently chiral and optically active, and thus will display n → π^* transitions having enhanced absorption and rotatory power.[58] Second, the magnitudes of the chiroptic properties of ketones **28** and **29** should be similar to one another but display Cotton effects of opposite signs if the proposed stereospecificity of the overall reaction is correct. Finally the chiroptic properties of these two ketones should be similar to those observed for similar bicyclic β,γ-unsaturated ketones[59] such as norbornenone (**13**).[60] The failure of any of these predictions would vitiate the proposed reaction pathway.

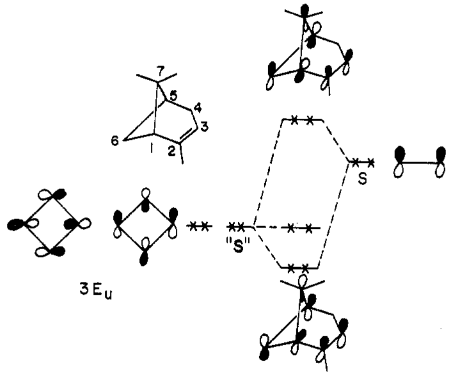

Figure 4. Molecular orbitals of α-pinene.

Indeed, all these predictions obtain.[23] As indicated by the molar extinction of the n–π^* transitions and the magnitude of the Cotton effect for each ketone, the isolated ketones are inherently chiral, having n → π^* transitions symptomatic of β,γ unsaturation. Further, postulated skeletal enantiomeric stereochemistry is indicated by the ultraviolet and circular dichroic spectra of ketones **28** and **29** being virtually superimposable in location and magnitude while the signs of the Cotton effects are opposite, as seen in Figure 3. Moreover, the predicted absolute configurations of ketones **28** and **29,** based upon the configuration of the pinene being treated, the sign of the ketone Cotton effect, and application of the octant rule, correlate with related ketones. Ring expansion from α-pinene is consistent with Scheme II.

The fact that pinene, a vinylcyclobutane, undergoes ring expansion while norbornene, a vinylcyclopentane, does not, must be understood. The highest occupied molecular orbital of α-pinene may be derived formally from the interaction of the π molecular orbital of the C=C fragment with one of the two degenerate 3E$_u$ Walsh molecular orbitals[55] of the cyclobutane fragment (Figure 4). This interaction raises the energy of the α-pinene HOMO in comparison to those of its component fragments, thus enhancing the electron-donor properties of α-pinene. This frontier molecular orbital has the correct symmetry to transform into an allyl residue at C-1–C-3. The node between C-1 and C-6 and the attendant bond weakening are in line with migration of the C-6–C-1 bond to a metal center placed underneath the C-1–C-3 allyl residue. A similar argument with norbornene does not obtain as the appropriate cyclopentane orbital is far lower in energy than the cyclobutane orbital.

Conclusion

Even though these carbonylation reactions are as yet not completely understood, they are highly stereospecific and therefore of great potential use. Synthetic chemists look to organometallic systems for new reactions: carbon–carbon bond formation is a prime example. Often coupling reactions have a radical character and are rather indiscriminate, leading to a variety of products. The Fe(CO)$_5$-mediated carbonylation of olefins is an efficient process: conventional routes to many of the compounds reported here would be cumbersome. Yet the molecules obtained, sometimes with high enantiomeric purity, have interesting structures.

The task ahead of us is to devise reaction conditions, and to choose appropriate ancillary ligands, to facilitate

[56] S. W. Tam, *Tetrahedron Lett.*, 2385 (1974).

[57] R. M. Moriarty, K. N. Chen, M. R. Churchill, and S. W. Y. Chang, *J. Am. Chem. Soc.*, **96**, 3661 (1974).

[58] (a) D. A. Lightner and W. A. Beavers, *J. Am. Chem. Soc.*, **93**, 2677 (1971), and references cited therein; (b) K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, New York, N.Y., 1966, p 158.

[59] A. Moscowitz, K. Mislow, M. A. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

[60] See D. I. Sandman and K. Mislow, *J. Org. Chem.*, **33**, 2924 (1968), and references cited therein.

successful cyclopentanone formation from olefins as a general process. It may also prove possible to control product stereochemistry by suitable selection of carbonylating agents. Implicit in the proposed reaction pathways is the development of catalytic carbonylations.

We gratefully acknowledge our debt to collaborators who carried out the experiments which have been described. As graduate students at Wesleyan University and at Princeton University, respectively, Dr. John Mantzaris and Dr. Arnold Speert studied the cyclopentanone formation from strained ring hydrocarbons. Dr. Alan P. Marchand worked on olefin coupling during a sabbatical year spent at the University of Liège in 1972–1973. Mr. Armel Stockis studied the enantiomeric recognition coupling of norbornenone at Liège, and while on a NATO-funded exchange at Wesleyan investigated the ring expansion of the pinenes. Mr. George Page has studied the enantiomeric recognition of 2-methylenenorbornene at Wesleyan. Our thanks go to the NATO Scientific Affairs Division for funding a collaborative venture by E.W. and P.L. E.W. thanks the Research Corporation for financial support and BASF for a gift of Fe(CO)$_5$; P.L. thanks the Founds de la Recherche Fondamentale Collective for a grant toward the purchase of the Bruker HFX-90 nmr spectrometer.

σ-Bonded Organic Derivatives of f Elements

Minoru Tsutsui,* Neal Ely, and Ronald Dubois

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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A new and exciting aspect of organometallic chemistry has been unveiled with the successful synthesis of a series of σ-bonded derivatives of the f elements. The f elements are the 14 elements that follow lanthanum and actinium in the periodic table and in which the 4f and 5f electrons are sequentially added to either the lanthanum or the actinium configuration. This Account deals with recent advances made in the synthesis and characterization of σ-bonded alkyl and aryl derivatives of organolanthanide and actinide compounds.

Because the lanthanide and actinide ions have such unique electronic and stereochemical properties, the synthesis of their σ-bonded derivatives has been a long-sought goal. The possible f-orbital participation in bonding, coupled with the unusually high coordination numbers and resultant coordination geometries, suggest that these compounds possess intriguing potential as organometallic reagents and catalysts. By providing the correct coordination geometries for the reacting species, a coordinatively unsaturated σ-bonded organic derivative of an f element can catalyze various chemical transformations.

The belief that σ-bonded organic derivatives of f elements could become important organometallic reagents and catalysts finds overwhelming support in the chemistry of σ-bonded organic derivatives of d-block transition metals. The current literature[1] reveals a large number of transition-metal-catalyzed processes of both industrial and biological significance which involve the use of a σ-bonded organometallic derivative as the active catalyst. Preliminary reports by Lugli et al.[2a] and Marks[2b] have shown that σ-bonded organoactinide (Cp_3UR, $Cp = \eta^5\text{-}C_5H_5$ and R = Me, Ph, $PhCH_2$) complexes can act as catalysts in olefin oligomerization reactions and as templates in cyclooligomerization reactions. These studies heighten our hopes that the investigation of these new types of organometallic derivatives may lead to more selective and efficient catalysts.[2c]

Historical Background

Although attempts to synthesize organometallic derivatives of group 3B elements date back to Pletz[3a] in the late 1930's and to Gilman and Jones[3b] in the mid 1940's, the first successful synthesis of π-bonded organometallic compounds of the lanthanides[4a] and actinides[4b] was reported by Wilkinson et al. in the mid 1950's. In spite of a surge of interest in the early 1960's when a series of π-bonded cyclopentadienyl derivatives of the rare earth elements was reported,[5–9] the field remained relatively dormant until 1968 when Streitwieser et al.[10] reported the successful synthesis of ura-

Minoru Tsutsui, a native of Japan, received a B.A. degree from Gifu University in Japan, M.S. degrees from both Tokyo University of Literature and Science and Yale University, and a Ph.D. degree from Yale in 1954. He has been on the staff at Tokyo University, Monsanto Chemical Co., and New York University. Since 1968 he has been Professor of Chemistry at Texas A&M University. His research interests include organotransition-metal chemistry, the chemistry of novel metalloporphyrins, homogeneous catalysis, one-dimensional conductors, and diagnostic and chemotherapeutic agents.

Neal M. Ely was born in Dallas, Texas. He received the Ph.D. degree from Texas A&M in 1974 with Professor Tsutsui, and much of the work described in this Account is based on his dissertation project.

Ronald Dubois is a Robert A. Welch Postdoctoral Fellow at Texas A&M. He was born in New Bedford, Mass., and received the Ph.D. degree from the University of Hawaii in 1975.

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(1) (a) M. Tsutsui, *Ann. N.Y. Acad. Sci.*, **93**, 33 (1961); (b) M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *Angew. Chem., Int. Ed. Engl.*, **8**, 410 (1969); (c) M. Tsutsui and C. E. Hudman, *Trans. N.Y. Acad. Sci.*, **34**, 595 (1972), and reference therein; (d) M. Tsutsui and E. I. Becker, Ed., "Organometallic Reactions", Vol. 1–4, Wiley, New York, N.Y., 1972; (e) M. Tsutsui and Y. Ishii, Ed., "Organotransition-Metal Chemistry", Plenum Press, New York, N.Y., 1975.

(2) (a) G. Lugli, A. Mazzei, and S. Poggio, *Makromol. Chem.*, **175**, 2021 (1974); (b) T. J. Marks in "Organotransition-Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, pp 81–91; (c) For a review of the catalytic behavior of some uranium derivatives see E. Cernia and A. Mazzei, *Inorg. Chim. Acta*, **10**, 239 (1974).

(3) (a) W. M. Pletz, *C. R. (Dokl.) Acad. Sci. URSS*, **20**, 27 (1938); (b) H. Gilman and R. G. Jones, *J. Org. Chem.*, **10**, 505 (1945).

(4) (a) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956); (b) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 246 (1956).

(5) E. O. Fischer and Y. Hristidu, *Z. Naturforsch.*, **176**, 275 (1961).

(6) E. O. Fischer and A. Trieber, *Z. Naturforsch.*, **176**, 276 (1961).

(7) (a) R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963); (b) S. Manastyrskyj, R. E. Maginn, and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).

(8) G. L. Ter Haar and M. Dubeck, *Inorg. Chem.*, **3**, 1648 (1964).

(9) M. Tsutsui, T. Takino, and D. Lorenz, *Z. Naturforsch.*, **216**, 1 (1965).

(10) A. Streitwieser, Jr., and U. Muller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).